Interaction between Finite-Sized Particles and End Grafted Polymers

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ABSTRACT: We describe the deformation behavior of polymer brushes and mushrooms compressed by finite-sized particles for the cases where the chains are fixed or mobile on the grafting surface. When the size of the particle is large compared to the grafting distance of the chains, the force on the particle is the same to lowest order in compression for both the fixed and surface mobile chains. Compression of a single mushroom can lead to a first order like escape transition, where part of the chain escapes from under the particle. These transitions can be seen either in the chain radius or in the compressional force law behavior. For surface mobile mushrooms, the force is considerably smaller because of the evacuation of chains from under the particle. The force law in this case also exhibits a maximum at a certain compression, indicating that the system undergoes a collapse transition above a critical pressure or yield stress $P_c \approx kT\sigma_0 R_{F3}^{-1}$, where σ_0 is the grafting density (chains/area) and R_{F3} is the unperturbed mushroom size. Finally, we consider the case of bending of stiff chains grafted to a solid surface. In the case of a single chain, the force is a constant for weak compressions. In the multichain case, the force can be substantially lower because of the escape of chains from under the particle.

1. Introduction

The subject of grafted polymers at the interfaces of cells, liposomes, and colloids is currently receiving considerable attention, particularly in connection with sterically stabilized liposomes used for drug delivery.[1,2] Recent experiments have shown that, by grafting polymers on liposomes, the circulation time of liposomes in the blood stream can be substantially increased, resulting in enhanced drug delivery properties.[3] At low grafting densities (chains/area) in a good solvent the chains form individual "mushrooms". At high enough grafting densities the grafted polymers form "brushes" whose height scales linearly with the molecular weight of the polymers. In both cases the grafting of the chains gives rise to a number of interesting properties. A detailed understanding of the properties of grafted polymers will allow improved methods of colloid stabilization, the design of biosurfaces with tailored properties, and the creation of new copolymer alloys.

Although the literature on polymer brushes is large,[4−6] most theoretical studies to date have focused on equilibrium properties such as the layer height, monomer concentration profile, and end density distribution of polymer chains.[4,7−9] Studies on the deformation behavior of brushes in nontrivial geometries are relatively sparse and have been confined to molten polymer brushes on a solid surface where the grafting density is fixed.[10−16] In this paper we study the deformation behavior of polymer brushes grafted on both solid and liquid surfaces. The term solid brush is employed to denote the case of grafted polymers on a surface where the grafting sites are immobile. Similarly, for a liquid brush the grafting sites are mobile, although the total number of chains on the surface is fixed. In this paper the surface is always flat and cannot bend. The motivation for this study stems in part from the wide-ranging applications of grafted chains in biophysics including cell adhesion and interactions of polymer coated liposomes and vesicles with cells, proteins, and colloidal particles. For these applications the liquid brush case is the most relevant.

In this paper we consider a number of situations which may occur when grafted chains interact with a finite-sized particle. In section 2, we consider the deformation of a solid brush by a particle using the self-consistent field theory for the energy of a compressed brush[17] and extend the calculation to the case of a liquid brush. We find that the force on the particle is the same in both the solid and liquid brushes to first order in the extent of deformation. The force on the particle is weaker in the liquid brush if higher order terms in the deformation are taken into account. We then study the deformation behavior in the "mushroom" regime (where the grafting distance is greater than the radius of gyration of the chains) in section 3, for both solid and liquid grafting surfaces. We find a novel "escape" transition for a single mushroom on a solid surface.[18] When many polymer coils are grafted to a liquid surface, an additional term due to the translational entropy of the coils has to be taken into account. In that case the mushrooms can partially evacuate the region under the disk. This effect gives rise to a force law which has a maximum as a function of compression. At large compressions the force felt by the compressing particle decreases due to chain evacuation. Finally, in section 4, we study brushes made of wormlike chains with length somewhat less than a persistence length. Many polymers of biological importance are of this type. Such chains pay a bending penalty for compression and exhibit compression force laws very different from those of more flexible chains.

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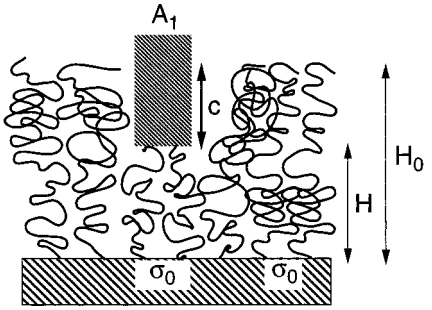

Figure 1. Side view of a solid brush compressed by a particle of cross sectional area A_1. The surface density σ_0 is a constant in this case. The extent of penetration is denoted by c, and the unperturbed height of the brush is H_0. In our model the chains undergo pure compression and the chains outside the region of the particle remain unperturbed.

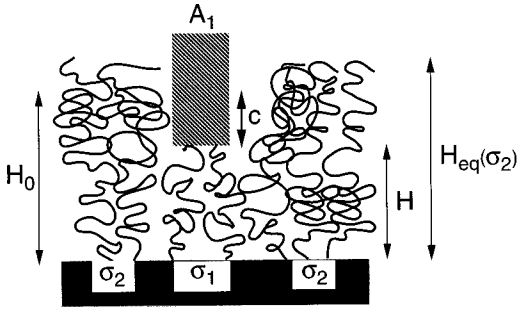

Figure 2. Side view of a liquid brush compressed by a particle of cross sectional area A_1. The region under the particle has a grafting density σ_1 while the rest of the brush has a grafting density σ_2. The equilibrium height $H_{eq}(\sigma_2)$ is different from H_0 because σ_2 is not equal to the unperturbed grafting density, σ_0.

2. Deformation Behavior of Brushes

2.1. Solid Brush. In this and the following section we consider the interaction of brushes of flexible polymers with finite-sized particles. There are two alternative approaches for studying such brushes. The oldest approach due to Alexander and de Gennes[7] assumes that all the chain ends are localized at the tip of the brush. The volume fraction of polymer within the layer is thus assumed to be constant. The more recent self-consistent field (SCF) approach developed by several authors[8,9] relaxes this assumption. These calculations yield a parabolic profile for the volume fraction of monomers. Both the Alexander−de Gennes model and the SCF calculations yield the same scaling behavior for the equilibrium height of the brush and the free energy. However, the Alexander−de Gennes model predicts a lower brush height and a higher free energy than the SCF model. For many situations of interest the former approach is more appealing since it is simple and gives correct results within numerical prefactors. However, for certain measurements, of which brush compression is one, the SCF theories give more accurate results, and we use the results obtained from them here. We consider a solid brush with a fixed total area A and a grafting density σ_0 (chains/area). The brush is assumed to be in a "not too good" solvent such that the self-consistent mean field calculations are applicable.[8] Here we consider for simplicity a cylindrical particle of constant cross sectional area A_1 (Figure 1). The unperturbed height of the brush is denoted by H_0 and the free energy per unit area by f_0. The equilibrium brush height and free energy per unit area are $H_0 \approx Na(a^2\sigma_0)^{1/3}$ and $f_0 \approx N\sigma_0(a^2\sigma_0)^{2/3}$, where N is the degree of polymerization of the chains, a is the monomer size, and σ_0 is the grafting density. The free energy per unit area of the brush upon compression to a height H is given by[17]

$$f(\sigma,H) = f_0(1/u + u^2 - u^5/5) \qquad (1)$$

$$u = H/H_{eq}(\sigma)$$

where H is the height of the compressed brush and H_{eq} is the equilibrium height at the given surface grafting density, σ_0. For a solid brush, H_{eq} is equal to H_0 since there is no change in the grafting density upon deformation. The particle compresses the chains beneath it to a height H. The remaining chains in the brush are assumed to be unaffected by this compression. Furthermore, we assume that the chains undergo pure compression and do not splay upon deformation by the particle[19] (Figure 1). With these assumptions, the total free energy of the system is given by a simple sum of the free energy of the region under the particle and the remainder of the surface

$$F = A_1 f(\sigma_0,\mathrm{H}) + (A - A_1)f(\sigma_0,H_0) \qquad (2)$$

In most real situations the area of the particle will be much smaller than the area of the brush, $A_1 \ll A$. Expanding the total free energy to first order in A_1/A, and also expanding in c/H_0, we get

$$F = Af_0[1 + {}^5/_3(A_1/A)(c/H_0)^3 + {}^2/_3(A_1/A)(c/H_0)^5 + {}^5/_9(A_1/A)(c/H_0)^6(1/(1-(c/H_0)))] \qquad (3)$$

where $c = H_{eq} - H$ is the extent of compression of the brush. The force exerted by the brush on the particle is just $-(\mathrm{d}F/\mathrm{d}c)$. The force is always repulsive as expected and scales with c^2 to the lowest order in c/H_0.

2.2. Liquid Brush. In analyzing the deformation behavior of a liquid brush, the mobility of the chains on the surface has to be taken into account. Nevertheless, the chains are still assumed to be grafted to the surface, and the number of chains is fixed. The mobility of the chains results in a variation in grafting density. We employ the following simplifying assumptions in treating the liquid brush deformation: (a) the chains are considered to undergo only pure compression and do not splay (as in the previous case), and (b) the variation in the grafting density is taken into account by considering a uniform grafting density σ_1 in the region under the particle and a uniform grafting density outside the region of the particle σ_2 (Figure 2). The second assumption is a primitive way of modeling the chain mobility on the surface. In practice, the grafting densities, σ_1 and σ_2, are different from the original unperturbed grafting density, σ_0. The values of σ_1 and σ_2 are determined by minimizing the total free energy of the system subject to the constraint of the conservation of the total number of chains

$$A_1\sigma_1 + (A - A_1)\sigma_2 = A\sigma_0 \qquad (4)$$

The total free energy of the system is given by

$$F = A_1 f(\sigma_1,H) + (A - A_1)f(\sigma_2,H_{eq}(\sigma_2)) \qquad (5)$$

$H_{eq}(\sigma_2)$ refers to the equilibrium height of the brush at the grafting density σ_2. This height will be different than the unperturbed height of the brush in the absence

of deformation because σ_2 is different from σ_0. Minimizing eq 5, taking into account the constraint of the conservation of chains (eq 4), yields

$$\sigma_1 = \sigma_0(1 - {}^3/_2(c/H_0)^2 + {}^1/_2(c/H_0)^3) \quad (6)$$

and the corresponding free energy is (again to first order in A_1/A)

$$F = Af_0[1 + {}^5/_3(A_1/A)(c/H_0)^3 - {}^5/_4(A_1/A)(c/H_0)^4 + O((c/H_0)^5)] \quad (7)$$

to lowest orders in c/H_0. c is the extent of compression of the brush and is equal to $H_0 - H$. Comparing eqs 3 and 7 for the free energy of deformation for a solid and liquid brush, respectively, we see that, to lowest order in c/H_0, the free energy and hence the force on the particle are the same in both the solid and liquid brush cases. However, at order $(c/H_0)^4$ the energy of a liquid brush is lower. In the liquid brush, the chains can relieve the compression imposed by the particle by moving out of the region of deformation. This is clear from our expression for the grafting density σ_1 (eq 6) which indicates a lowering of the grafting density upon deformation. Note that, in both the solid and liquid brushes, the force on the particle is always repulsive and increases with increasing deformation, i.e., increasing c.

3. Deformation of Mushrooms

3.1. The Solid Mushroom Regime. Recently, the deformation behavior of individual polymer coils grafted to a surface have been studied where the deformation was caused either by electric fields[20] or flow.[21] In this and the next section we discuss the compressional behavior of less densely grafted chains. These chains form individual mushrooms which interact only very weakly with their neighbors. As in the brush regime, we can study both the solid and liquid cases interacting with finite-sized particles. The liquid case is the simplest and possibly the most relevant to biological systems, but the solid case shows much richer behavior. The problem is treated in detail in ref 18, and we only briefly review the results here. We analyze the different cases using blob arguments *ignoring numerical prefactors*.

The simplest problem to discuss is that of a single coil, permanently grafted directly beneath the center of a disk of radius R which compresses the mushroom. The radius of the undeformed mushroom is given by the Flory formula $R_{F3} = aN^{3/5}$. We assume that $R_{F3} < R$ so the particle completely covers the mushroom. If the height of the disk above the grafting surface D is less than R_{F3}, the chain is strongly compressed and forms a string of "blobs"[22] with an associated energy $F = kTN(a/D)^{5/3}$. One way in which the chain can relieve the compression is to partially escape from beneath the disk. Of course, the center of each chain is tethered so it cannot completely escape. The means of escape which has the lowest free energy is to form a straight tether composed of R/D blobs from the center to the outside of the disk.[18] Outside the disk a large blob is formed from the remaining monomers (Figure 3) with an associated energy kT which we ignore. The condition for escape is obtained by equating the stretching energy required to form the tether, $F = kT(R/R_{F2})^4$, and the energy of the totally confined chain, $F = kTR/D$.[18] $R_{F2} = D(R/D)^{3/4}$ is the two-dimensional Flory radius of the chain.

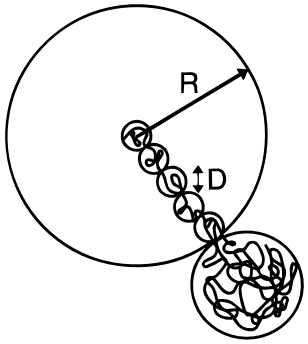

Figure 3. Top view of a mushroom after escape. The chain forms a string of R/D blobs under the disk, and the remaining monomers form one large blob outside the disk.

The escape transition occurs at a value of D given by

$$D^* = aN^{3/2}(a/R)^{3/2} \quad (8)$$

Even though for $D < D^*$ the escaped state has lower free energy, there is usually an energy barrier for the chain to overcome in order to escape. Moreover, the chain exhibits hysteretic behavior on compression and decompression.[18] The force law for the escaped chains scales as D^{-2}. In effect, we have a first order like escape transition. The hysteretic behavior can be observed in both the chain radius and the force law. Extending the analysis to a noninteracting many mushroom case leads to a modified force law because of the presence of escaped chains.[18]

3.2. The Liquid Mushroom Regime. The calculation for the liquid mushroom regime proceeds as follows. Unlike the solid mushroom case, a single liquid mushroom does not show any interesting escape transitions because of the mobility of the grafting point. Here, we consider the situation of many noninteracting mushrooms grafted to a liquid surface. We assume, as before, that the compressing particle is a disk of radius R and area $A_1 = \pi R^2$ much larger than a mushroom size $R_{F3} = aN^{3/5}$, and that the disk originally covers many mushrooms, so that $A_1\sigma_0 \gg 1$. Since the number of chains is conserved, we have the constraint (eq 4). As before, we assume that under the disk there is a constant density of mushrooms σ_1 and outside the disk another constant density σ_2. The total free energy consists of the energy needed to compress the mushrooms plus the "ideal gas" translational entropic terms of the grafted coils. These latter terms mean that when the mushrooms are compressed, those under the disk do not simply all evacuate. There is always a small "ideal gas" pressure forcing some mushrooms under the disk. The total free energy in the limit of low grafting densities $\sigma R_{F3}^2 \ll 1$

$$F/kT = \sigma_1 A_1 N(a/D)^{5/3} + \sigma_1 A_1 \ln \sigma_1 + \sigma_2(A - A_1)\ln \sigma_2 \quad (9)$$

and taking into account the constraint (eq 4) and minimizing with respect to σ_1 gives

$$\sigma_1 = \sigma_0 A/A_1[\exp(-N(a/D)^{5/3})/(1 + \exp(-N(a/D)^{5/3}))] \quad (10)$$

and a free energy of

$$F/kT = \sigma_0 A_1[1 - \exp(-N(a/D)^{5/3})] \quad (11)$$

The force is then

$$p = kT\sigma_0 A_1 N(a^{5/3}/D^{8/3}) \exp(-N(a/D)^{5/3}) \quad (12)$$

Physically, we can recognize this force as the force needed to compress a solid mushroom system, but with an exponetially small prefactor which accounts for the evacuation of the mushrooms from under the disk. Note that although the energy gets larger at smaller D, the force shows a maximum and gets smaller for smaller D. Thus the system is easy to compress at first and then gets more difficult, and then at stronger compressions it becomes much softer. This system thus shows "compression-thickening" followed by "compression-thinning" behavior. Ultimately, this means that the system shows a yield stress P_c given by $P_c \sim kT\sigma_0 R_{F3}^{-1}$. Below this stress the system gets compressed somewhat. Above this stress the system becomes totally squashed.[18]

Another situation of interest in the liquid mushroom arises when the disk has an attractive van der Waals interaction with the grafting surface. Considering only the van der Waals interaction between the disk and surface, we get the attractive energy $F_{vdw} \sim -AV_p/D^3$, where AkT is the Hamaker constant[23] and V_p the volume of the particle. If t is the thickness of the particle, then V_p is given by $V_p = tA_1$. The presence of van der Waals energy implies that the absolute minimum is always at the grafting surface because of the infinite potential well introduced by the van der Waals interaction. Adding the van der Waals energy to the deformation energy and minimizing the total free energy result in the existence of a maximum in the bulk, indicating that the particle has to overcome an energy barrier to reach the absolute minimum (at the grafting surface). Thus we do not have a first order phase transition, but the system does exhibit hysteresis because of the presence of an energy barrier. The position of the bulk maximum depends on the dimensionless parameter $At/\sigma_0 R_{F3}^3$. The bulk maximum disappears above a critical value of $At/\sigma_0 R_{F3}^3 = 0.2$. For most cases of interest, A is usually of the order of 40, and if we take $t = 0.1R_{F3}$ and $\sigma_0 = R_{F3}^{-2}$, we get $At/\sigma_0 R_{F3}^3 = 4$, somewhat larger than the critical value. This implies that the bulk maximum is never present for many real situations and also shows the inffectiveness of mobile mushrooms in providing a steric barrier to the particle.

4. Compression of a Stiff Brush

In the previous sections we have considered flexible chains attached to a surface. It is useful to compare this with the case of fairly rigid or wormlike chains which can bend but have difficulty extending. Such chains are very prevalent in biological systems. For instance, cells contain large quantities of actin, DNA, spectrin, and microtubules.[24] These materials all have significant bending moduli and are often present as short segments of the order of one persistence length. Such chains behave very differently when compared with more flexible polymers. For instance, they readily form liquid-crystalline phases.[25] Here, we study the problem of grafted rigid chains undergoing pure bending deformation. Brushes composed of such chains occur for instance in the Desomosones linking cells[24] although in that case they probably have an adhesive function. We assume that the chains are grafted at right angles to the surface and that this angle is fixed. The free energy of a stiff elastic chain can be expressed as

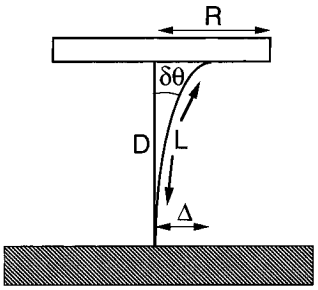

Figure 4. Side view of the bending of a stiff chain which is totally confined within the disk. The average tilt angle, $\delta\theta$, is assumed to be small. The chains are grafted at a fixed angle of 90° to the surface.

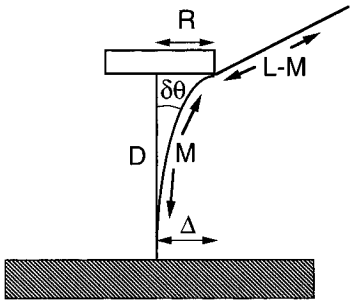

Figure 5. Escape of a stiff chain upon bending. The part of the chain beyond the region of the disk does not undergo any bending.

$$F = (\kappa/2)\int_0^L ds\ (d\theta/ds)^2 \approx (\kappa/2)L(\delta\theta/L)^2 \approx \kappa(\delta\theta)^2/(2L) \quad (13)$$

where L is the total arc length of the chain and $\theta(s)$ measures the angular deviation of the chain from the normal to the surface. $\delta\theta$ is some average tilt angle (Figure 4), and κ is a bending constant with units of energy times length. The persistence length of such a chain is κ/kT. Here, we require $\kappa/kT > L$ so that our chain is fairly rigid. Moreover, we use a two-dimensional model for the chain bending. In three dimensions a further angle is needed to describe the bending, but introduces no new physics. Suppose we take a single chain grafted to the surface. If there are no obstacles, the height of the chain tip is L and the chain points normal to the surface along its entire length. Now if we bring a large disk to within a distance $D < L$ of the surface, the chain is forced to bend. In principle, the bending energy can be solved exactly, but here we use the following approximate picture which gives the essential physics for small deformations. The rod is forced to bend though an average angle (see Figure 4) $\delta\theta = (1 - D/L)^{1/2}$ so that the bending energy of the rod is

$$F \approx \kappa(1 - D/L)/(2L) \quad (14)$$

This gives a force on the particle which is constant $p_{conf} = \kappa/2L^2$. Since we have $\kappa > LkT$, the force must be at least $kT/2L$. The deflection in the direction along the surface is $L\ \delta\theta = L(1 - D/L)^{/1/2}$.

Now consider the rod compressed by a disk of finite size. In this case, the rod can avoid a certain amount of bending by escaping from under the disk (Figure 5). Suppose the grafting site is a horizontal distance Δ from the edge of the disk. In the escaped configuration, it takes an arc length M to reach the edge. We thus have

the relations $M^2 = \Delta^2 + D^2$ and $\delta\theta \sim \Delta/D$, so that the bending free energy is $\kappa\Delta^2/D^3$ and the force is $\kappa\Delta^2/D^4$. Comparing the free energies in the escaped and imprisoned cases gives a critical value of Δ, $\Delta_c = L(1 - D/L)^{1/2}$. This is also the deflection experienced by an imprisoned chain. Note that in the escaped configuration the force changes drastically and has a much stronger dependence on D. At $\Delta = \Delta_c$, the ratio of the two forces is $1 - D/L \ll 1$. It is thus much easier to compress an escaped chain.

We can also extend this kind of analysis to the regime of many chains. Here we assume negligible interactions between the chains. If the chains are grafted with surface density σ and the disk has radius R, then we can divide the region under the disk into an unescaped core of radius $R - \Delta_c$ surrounded by an annulus of escaped chains. The free energy is

$$F \approx \sigma(R - \Delta_c)^2(\kappa/2L)(1 - D/L) + \sigma\int_{R-\Delta_c}^{R} r\, dr\, \kappa/(2D^3)\Delta^2 \quad (15)$$

where the first term denotes the free energy of confined chains and the second term represents the free energy of the escaped chains. The corresponding force is

$$p \approx p_{conf}(1 - 2L\epsilon^{1/2}/R) \quad (16)$$

where p_{conf} is the force due to completely confined chains and $\epsilon = (1 - D/L)$. Note that this force is lower than that for a completely confined system of chains. For somewhat stronger compressions, all the chains can escape ($R - \Delta_c = 0$) and the force is $p_{esc} = \sigma\kappa R^4/(8D^3)$.

Conclusions

In this paper we have considered a number of situations involving the deformation behavior of polymers grafted to a surface. A rich variety of behavior is observed depending on whether the surface is solid or liquid and whether the tethered chains are in the mushroom or brush regime. The deformation behavior of both solid and liquid brushes was studied using self-consistent mean field arguments. The self-consistent approach gives rise to a repulsive force which is identical for both solid and liquid brushes to first order in the extent of deformation, D. When higher order terms in the deformation are taken into account, we find that the repulsive force in the liquid brush is smaller. This result is intuitively obvious because in a liquid brush the chains can relieve the compressive force of the particle by moving out of the region of deformation. Our calculations were done perturbatively with respect to both the deformation of the brush and the area of the particle. This is usually the case of interest in biological systems where the particle is typically a protein whose dimensions are small compared to the grafting surface (such as cell membranes). In the above calculations, we have assumed that the particle purely compresses the brush without causing any splaying of the brush. This is an approximation which is likely to give reasonable results for small deformations. For large particles strongly compressing the brush it is likely to be innacurate, but improving it would require much calculational effort. One way of doing so for a melt brush was investigated recently.[14] This uses a hydrodynamic analogy which relies crucially on the incompressibility of a melt. In a polymer solution, where the blob size varies, it breaks down and there is no obvious generalization. Here, the variation in the surface grafting density of a liquid brush is also modeled in a primitive way. Improved methods of calculating the force should include the above two effects. Finally, real biological systems usually involve spherical or quasi−spherical particles. Treating such cases would be inherently more complicated than the simple cylindrical particle we have considered because of the geometry. Moreover, splaying of the chains would prove important for such systems. Nevertheless, our calculations should prove useful for a lowest order estimate.

The deformation behavior of mushrooms shows interesting transitions. For a single mushroom grafted to a surface, we find an escape transition at a certain compression, whereby part of the chain escapes from beneath the particle into the undeformed region. This transition also shows first order-like behavior because of the existence of an energy barrier to go from the confined to the escaped state. In the many mushroom case, we again find a critical deformation beyond which all the mushrooms are in the escaped state. For strong compressions, the force on the particle scales as D^{-2} for both the single mushroom and multimushroom systems.[18] When the mushrooms are grafted on a liquid surface, we find that the force on the particle is exponentially weaker than the solid mushroom system because of the mobility of the mushrooms on the surface. The total evacuation of the mushrooms is prevented by the "ideal gas" pressure of the mushrooms. The force also exhibits a maximum at some finite value of the deformation. This maximum occurs because of the competition between chain compression (which increases the force) and chain evacuation, which decreases the force. Beyond this deformation, the system is easy to compress, while for deformations smaller than the critical value, the system is difficult to compress. The maximum in the force could be identified with a "yield stress". The yield stress defines the value of the stress beyond which the mushrooms completely evacuate from beneath the particle.

Finally, we considered the deformation of stiff chains which undergo pure bending without any compression. For weak compressions of a single chain by a large disk, we found that the force on the particle was a constant irrespective of the degree of deformation. The interesting case occurs when the radius of the disk is small, allowing for the chain to escape from underneath the disk in order to lower the bending energy. In this case, the force was drastically lower than in the previous case of a completely confined chain and shows a strong dependence on the degree of deformation. We also extended the analysis to many chains grafted to a surface: a stiff brush. For a stiff brush deformed by a small disk, we calculated the force by considering a region where the chains are confined and an annulus of escaped chains. We obtained a reduction in the force compared to the case of totally confined chains, and the reduction can be substantial if L/R is large.

Despite their importance, direct measurements of the repulsive force exerted by a brush on a particle do not yet exist. There have been recent experiments on the repulsive forces between polymer grafted lipid bilayers by Tonya et al.[2] They have measured the forces both in the mushroom regime and in the brush regime. The bilayers in their experiments were in a glassy state, and consequently their system mimics a solid brush or a solid mushroom. In principle, our calculations can be tested using a blunt atomic force microscope tip by

measuring the force exerted by a brush on the tip of the microscope. The systems we have studied also lend themselves readily to computer simulations and are currently underway.

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